

AD-A043 091

BALLISTIC RESEARCH LABS ABERDEEN PROVING GROUND MD
X ALPHA CALCULATION OF TRANSITION ENERGIES IN MULTIPLY IONIZED --ETC(U)
JUL 77 D A RINGERS

F/G 20/8

UNCLASSIFIED

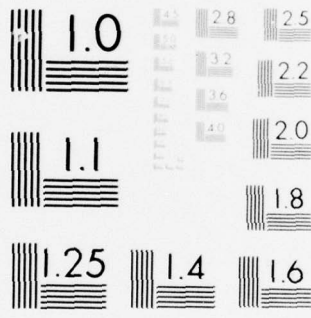
BRL-MR-2766

NL

1 OF 1
AD
A043 091



END
DATE
FILMED
9 -77
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

BRL MR 2766

BRL

AD

12
B.S.

AD A043091

MEMORANDUM REPORT NO. 2766

X_α CALCULATION OF TRANSITION ENERGIES
IN MULTIPLY IONIZED ATOMS

D. A. Ringers

July 1977

Approved for public release; distribution unlimited.

DDC
RECEIVED
AUG 22 1977
B

AD No. _____
DDC FILE COPY

USA ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
USA BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER BRL Memorandum Report, 2766	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) X _α Calculation of Transition Energies in Multiply Ionized Atoms		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) D.A. Ringers		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Ballistic Research Laboratory Aberdeen Proving Ground, MD 21005		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Materiel Development & Readiness Command 5001 Eisenhower Avenue Alexandria, VA 22333		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1L161102AH43
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 14p.		12. REPORT DATE JULY 1977
		13. NUMBER OF PAGES 16
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES *Portions of this work were performed while the author was a member of the Department of Physics, University of Oregon, where the work was supported by the US Army Research Office-Durham and by the National Aeronautics and Space Administration (Grant No. NGR-38-003-036).		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electronic Excitations, X-Alpha Method and Transition Energies		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (hmn) The X _α method has been applied to the calculation of ionization energies in multiply ionized atoms. It is shown that the accuracy of calculations can be improved if appropriate (different) values of α are used for each configuration. Alternatively, one can use the Slater transition state, wherein a total energy difference is related to a difference in single-electron eigenvalues. By a series expansion, the value of α for an excited configuration can be related to its value for the ground-state configuration. The terms $\Delta\alpha(\partial E/\partial\alpha)$,		

050 750

1B

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

→ thus introduced, exhibit a similar dependence on atomic number as the ground-state values of α . Results of sample calculations are reported and compared with experiment.


alpha

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

TABLE OF CONTENTS

	Page
I. INTRODUCTION.	5
II. THEORY.	5
III. RESULTS AND DISCUSSION.	7
IV. CONCLUSIONS	13
REFERENCES.	14
DISTRIBUTION LIST	15

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/EVALUATION CODES	
Dist.	SPECIAL
A	

I. INTRODUCTION

An increasing need has recently arisen for comprehensive theoretical work on transition energies, x-ray emission rates and Auger transition probabilities pertaining to multiply ionized atoms. Theoretical information on these atomic quantities is required to interpret a growing body of data derived from ion-atom collision experiments, beam-foil spectroscopy, data expected to arise from astrophysical processes¹, and data from experimental programs in combustion and erosion.

II. THEORY

In order to compute transition energies we have used the $X\alpha$ method². The $X\alpha$ eigenvalues and eigenfunctions agree closely with results from the Hartree-Fock (HF) method for closed-shell atoms and from the Hyper-Hartree-Fock (HHF) method for open-shell atoms³. And, with its local approximation to the exchange, the $X\alpha$ method leads to computational simplifications. The concept of the transition state⁴, whereby the ionization energy, a difference in total energy is well approximated by a single-electron eigenvalue, can be readily implemented in the $X\alpha$ theory. The transition-state concept avoids the necessity of carrying out two high-precision calculations, one for the initial-state total energy and one for the final-state total energy, which is usually necessary in the HF or HHF frameworks. Instead, it is possible to calculate directly a total energy difference. The $X\alpha$ method can also be extended to molecules and solids, whereas the HF method is in practice only useful for isolated atoms. It can be shown that Fermi statistics and the Hellman-Feynmann and virial theorems are inherently satisfied^{5,6}. The transition-state concept is finding increasing application and has been providing results in good agreement with experiment. So far, however, the method has not been utilized to achieve the accuracy of which it is capable. Thus, deviations of 10 eV from experimental binding energies of ~ 200 eV have been noted⁷. Considerable improvement is possible, as indicated below.

1. T. Bunch, L. Caroff, and Hans Mark, in Atomic Inner-Shell Processes, edited by B. Crasemann (Academic Press, New York, 1975).
2. Slater, J.C., Advances in Quantum Chemistry, edited by P.O. Lowdin, (Academic Press, New York, 1972).
3. Slater, J.C., Quantum Theory of Atomic Structure, Vol. 11, (McGraw-Hill, New York, 1960).
4. Slater, J.C., J. Phys. (Paris) 33, 1 (1972), for example.
5. Slater, J.C., Quantum Theory of Molecules and Solids. The Self-Consistent Field for Molecules and Solids, Vol. IV, (McGraw-Hill, New York, 1974).
6. Slater, J.C., J. Chem. Phys. 57, 2389 (1973).
7. Beebe, N.H.F., Chem. Phys. Lett. 19, 290 (1973).

Generally, in an atomic (or molecular, or solid) Slater transition-state calculation, a value of α for the neutral-atom ground-state configuration is used⁸. This procedure does not achieve the potential inherent in the method, particularly for inner shells. The problem lies in the fact that the value of α which is appropriate for the ground state is not appropriate for an ion with one or more inner-shell vacancies. In the X α theory, the total energy is a functional of α , and since the virial theorem expresses a relationship between the kinetic and potential energy of the system, one might expect different values of α to satisfy the virial theorem for the ground and excited states. To calculate the difference between the ground total energy $E_o(\alpha_o)$ and an excited-state total energy $E_e(\alpha_e)$, it is therefore necessary to relate the excited-state α_e to the ground-state α_o .

The original Slater transition-state concept for the process of ionization may be derived from an expansion of the total energy⁹ and can be expressed by the relation

$$E_o(\alpha_o) - E_e(\alpha_o) = \left. \frac{\partial E}{\partial n_i} \right|_r = \epsilon_i, \quad (1)$$

where ϵ_i is a single-electron eigenvalue of a state with occupation number halfway between the initial-state and final-state occupation numbers, and n_i is this occupation number, which formally need not be integral, evaluated at the reference state indicated by the subscript r . We expand

$$E_e(\alpha_e) = E_e(\alpha_o) + \Delta\alpha \frac{\partial E}{\partial \alpha}, \quad (2)$$

where $\Delta\alpha$ stands for the difference $\alpha_e - \alpha_o$. Taking account of the change in α , we therefore have

$$E_o(\alpha_o) - E_e(\alpha_e) = \epsilon_i - \Delta\alpha \frac{\partial E}{\partial \alpha}. \quad (3)$$

It has been common to use $E_e(\alpha_o)$ instead of $E_e(\alpha_e)$, neglecting the term $\Delta\alpha(\partial E/\partial \alpha)$; this is reasonable for outer shells. However, for inner shells it is often necessary to retain the additional term. In particular, this term cannot be neglected in calculations of Auger and Coster-Kronig

8. Schwarz, K., Phys. Rev. B 5, 2466 (1972).

9. Slater, J.C., and J.H. Wood, Int. J. Quant. Chem. tr, 3 (1970).

transitions, in which the energy of the emitted electron can be of the order of only a few eV. If neither the initial nor the final state is the ground state, two terms of the form $\Delta\alpha(\partial E/\partial\alpha)$ appear on the right hand side of Eq. (3).

III. RESULTS AND DISCUSSION

We have determined these additional terms and computed certain transition energies for a few multiply ionized atoms in order to test the approach. Preliminary calculations indicate that $(\partial E/\partial\alpha)$, while differing for each shell of a given atom, can be reasonably well approximated for most shells by the corresponding value calculated by Schwarz⁸ for neutral atoms. The factor $\Delta\alpha$ seems, from our preliminary calculations, to be a nearly linear function of Z for a given shell, behaving in much the same way as the ground-state α 's⁸ (Figs. 1-3).

Selected nonrelativistic values of $\Delta\alpha(\partial E/\partial\alpha)$ are listed in Table I. With these terms, relativistic binding energies were derived that agree quite well with measurements¹⁰ (Table II). As a further test of the method, we have calculated the energies of a few selected x-ray satellites and tentatively identified them with measured non-diagram, or satellite lines (Table III). A satellite line occurs near a relatively low lying energy level as a result of a rearrangement of the outer electrons.

Recent work¹¹ has indicated that the energy difference between the $K\beta'''$ satellite in aluminum, which has been attributed to a $KL_{2,3} \rightarrow L_{2,3}^M$ transition¹², and the $K\alpha$ satellite, which is due to a $KL_{2,3} \rightarrow (L_{2,3})^2$ transition¹³, should be equal to the energy of the $L_{2,3}$ satellite $(L_{2,3})^2 \rightarrow L_{2,3}^M$ and have a value of 15.2 ± 0.3 eV. Calculation of these transition energies by the $X\alpha$ method yields a value of 13.8 eV, which is in good agreement with the experimentally obtained value.

10. Siegbahn, K., C. Nordling, G. Johansson, J. Hedman, P.F. Heden, K. Hamrin, V. Gelius, T. Bergmark, L.W. Werme, R. Manne and Y. Baer, ESCA: Applied to Free Molecules, (North-Holland, Amsterdam, 1969).
11. Hanson, W.F. and E.T. Arkawa, Z. Physik **251**, 271 (1972).
12. Neddermeyer, H. and G. Wieck, Phys. Lett. **31A**, 17 (1970).
13. Horak, Z., Proc. Soc. (London) **A77**, 980 (1961).

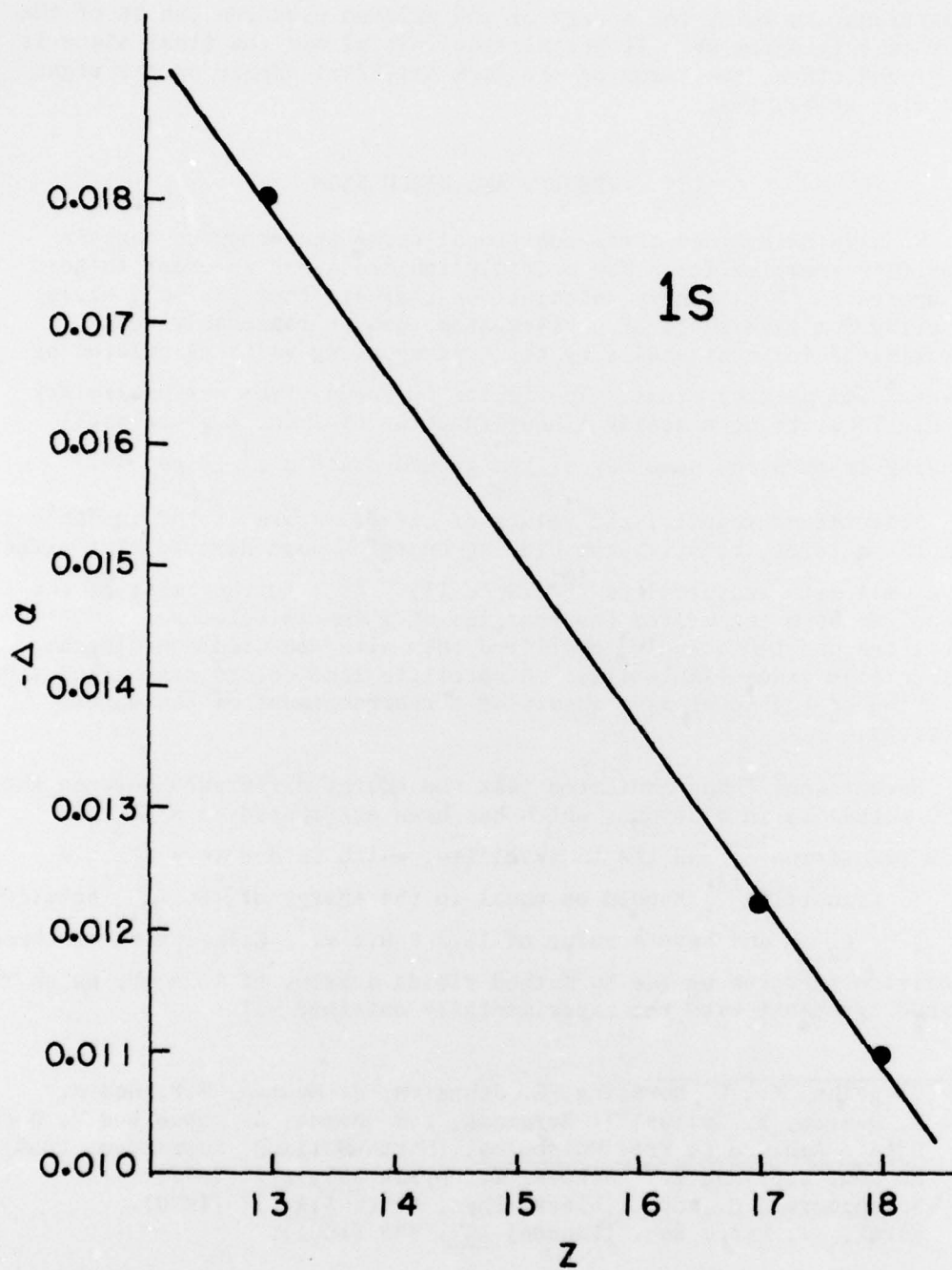


Figure 1. The term $\Delta\alpha$, as a function of Z , for the 1s shell of selected atoms for which the outermost electrons are in the 3p state.

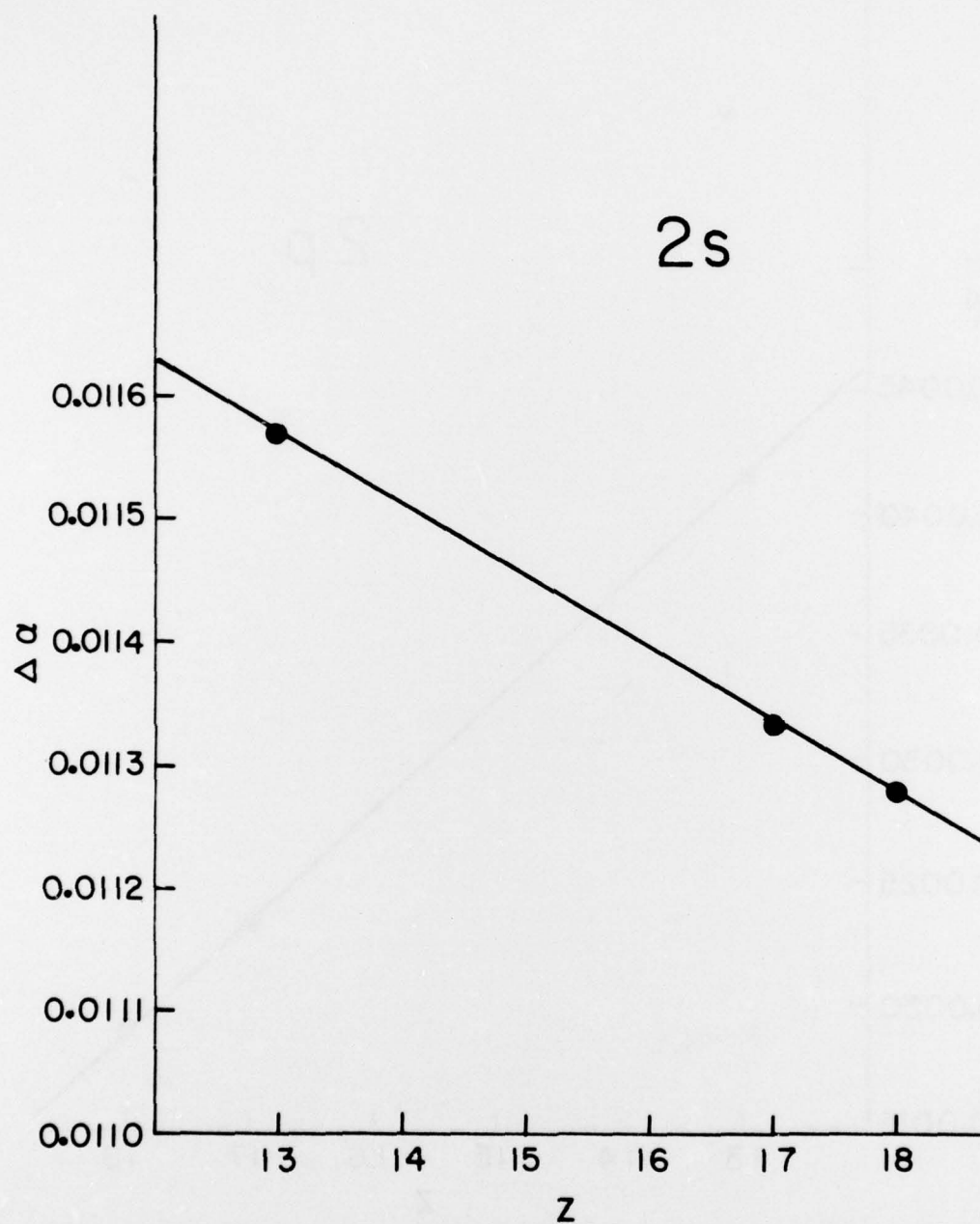


Figure 2. The term $\Delta\alpha$, as a function of Z , for the 2s shell of selected atoms for which the outermost electrons are in the 3p state.

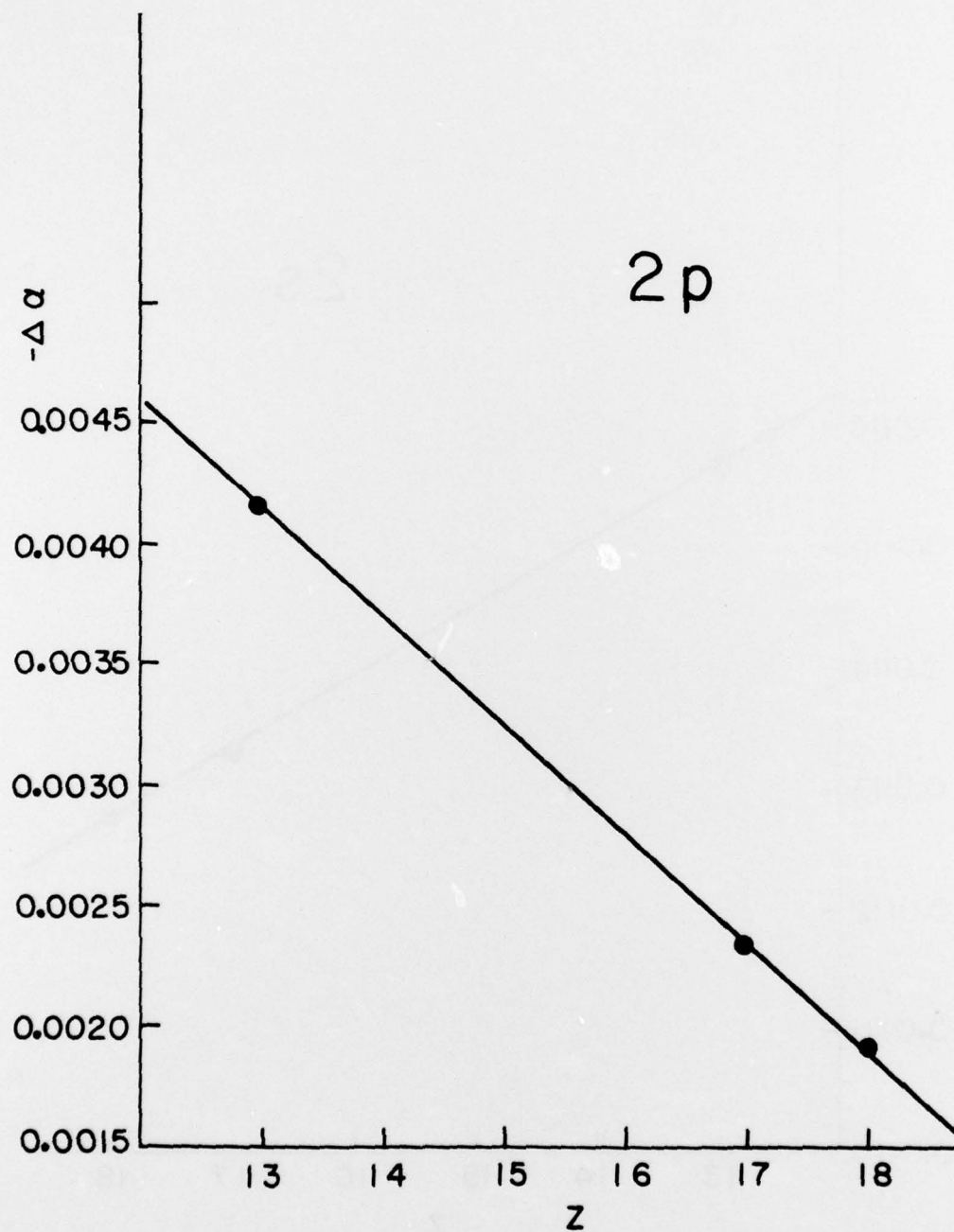


Figure 3. The term $\Delta\alpha$, as a function of Z , for the 2p shell of selected atoms for which the outermost electrons are in the 3p state.

Table I. Values of $\Delta\alpha(\partial E/\partial\alpha)$ for Selected Transitions.

Removed Electron	$\Delta\alpha(\partial E/\partial\alpha)$ (eV)		
	Al	Cl	Ar
1s	-9.81	-10.46	-10.41
2s	7.38	11.15	12.28
2p	-2.66	- 2.29	- 2.02
3s	-0.93	1.97	3.40
3p	0.23	- 0.74	- 0.81

Table II. Relativistic Binding Energies in Neutral Ar (in eV).

Electron	$\epsilon_i(\alpha_0)$	$\epsilon_i(\alpha_0) - \Delta\alpha \frac{\partial E}{\partial\alpha}$	Experiment ^a
1s	-3220.6	-3210.2	-3206.0
2s	- 314.8	- 327.0	- 326.3
$2p_{1/2}$	- 252.1	- 250.1	- 250.6
$2p_{3/2}$	- 250.1	- 248.1	- 248.5

^a Measured binding energies, from Ref. 10.

Table III. Experimentally Observed X-Ray Satellite Lines and Theoretically Derived Transition Energies in Multiply Ionized Atoms.

Element	Experiment			Theory ^a		
	Diagram Line	Satellite Line	Energy Difference (eV)	Initial Vacancy Configuration of Satellite	Final Vacancy Configuration of Satellite	Energy Shift With Respect to Diagram Lines (ev)
Al	K α_2	K α'	5.69	1s2p	$3p\ 2p, 2p$	6.90
	K α_2	K α_4	11.85	1s2p	$1d\ 2p, 2p$	12.00
	K α_2	K α_5	19.71	1s2p	$1s\ 2p, 2p$	19.63
	K α_2	K α_6	23.56	1s2p	$2p, 3s$	23.15
Cl	K α_2	K α'	10.73	1s2p	$3p\ 2p, 2p$	10.92
	K α_2	K α_3	17.44	1s2p	$1p\ 2p, 2p$	18.24
	K β_1	K β^v	2.44	1s3p	$3p\ 3p, 3p$	2.36
Ar	K $\beta_{1,3}$	K β''	8 ^b	1s3p	$1s\ 3p, 3p$	7.20
	K $\beta_{1,3}$	K β^v	3.3	1s3p	$1d\ 3p, 3p$	3.80

^a

Present work.

^b Scaled from graph in Ref. 14.

14. Druyvesteyn, M.J., Z. Physik 43, 707 (1927).

15. Ford, O.R., Phys. Rev. 41, 577 (1932).

16. Larkins, F.P., J. Phys. B4, 1 (1971).

IV. CONCLUSIONS

A consideration of the appropriate value of the exchange-correlation parameter for each configuration leads to improved results for ionization energies in multiply ionized atoms, when calculated by the formalism of the $X-\alpha$ theory. The terms $\Delta\alpha$ vary with atomic number in a manner similar to the variation of the ground state α values.

REFERENCES

1. T. Bunch, L. Caroff, and Hans Mark, in Atomic Inner-Shell Processes edited by B. Crasemann (Academic Press, New York, 1975).
2. Slater, J.C., Advances in Quantum Chemistry, edited by P.O. Lowdin, (Academic Press, New York, 1972).
3. Slater, J.C., Quantum Theory of Atomic Structure, Vol. II, (McGraw-Hill, New York, 1960).
4. Slater, J.C., J. Phys. (Paris) 33, 1 (1972), for example.
5. Slater, J.C., Quantum Theory of Molecules and Solids. The Self-Consistent Field for Molecules and Solids, Vol. IV, (McGraw-Hill New York, 1974).
6. Slater, J.C., J. Chem. Phys. 57, 2389 (1973).
7. Beebe, N.H.F., Chem. Phys. Lett. 19, 290 (1973).
8. Schwarz, K., Phys. Rev. B 5, 2466 (1972).
9. Slater, J.C., and J.H. Wood, Int. J. Quant. Chem. 54, 3 (1970).
10. Siegbahn, K., C. Nordling, G. Johansson, J. Hedman, P.F. Heden, K. Hamrin, V. Gelius, T. Bergmark, L.W. Werme, R. Manne and Y. Baer, ESCA: Applied to Free Molecules, (North-Holland, Amsterdam, 1969).
11. Hanson, W.F. and E.T. Arkawa, Z. Physik 251, 271 (1972).
12. Neddermeyer, H. and G. Wieck, Phys. Lett. 31A, 17 (1970).
13. Horak, Z., Proc. Soc. (London) A77, 980 (1961).
14. Druyvesteyn, M.J., Z. Physik 43, 707 (1927).
15. Ford, O.R., Phys. Rev. 41, 577 (1932).
16. Larkins, F.P., J. Phys. B4, 1 (1971).

DISTRIBUTION LIST

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
12	Commander Defense Documentation Center ATTN: DDC-TCA Cameron Station Alexandria, VA 22314	1	Commander US Army Armament Materiel Readiness Command Rock Island, IL 61202
1	Commander US Army Materiel Development and Readiness Command ATTN: DRCDMA-ST 5001 Eisenhower Avenue Alexandria, VA 22333	3	Commander US Armament Research and Development Command ATTN: Dr. J. Sharma, Dr. T. Gora Dr. P. Kemmey Dover, NJ 07801
1	Commander US Army Aviation Systems Command ATTN: DRSAB-E 12th and Spruce Streets St. Louis, MO 63166	1	Commander US Army Harry Diamond Labs ATTN: DRXDO-TI 2800 Powder Mill Road Adelphi, MD 20783
1	Director US Army Air Mobility Research and Development Laboratory Ames Research Center Moffett Field, CA 94035	1	Director US Army TRADOC Systems Analysis Activity ATTN: ATAA-SA White Sands Missile Range NM 88002
1	Commander US Army Missile Research and Development Command ATTN: DRDMI-R Redstone Arsenal, AL 35809	1	National Science Foundation Division of Materials Research ATTN: Dr. J.W.D. Connolly 1800 G Street Washington, DC 20550
1	Commander US Army Tank Automotive Development Command ATTN: DRDTA-RWL Warren, MI 48090	1	Northwestern University Physics Department ATTN: Prof. D.E. Ellis Evanston, ILL 60201
2	Commander US Army Mobility Equipment Research & Development Command ATTN: Tech Docu Cen, Bldg 315 DRSME-RZT Fort Belvoir, VA 22060	3	University of Florida Quantum Theory Project ATTN: Dr. Brett Dunlap Prof. J. Sabin Prof. S. Trickey Williamson Hall Gainesville, FL 32611

DISTRIBUTION LIST

<u>No. of Copies</u>	<u>Organization</u>
1	University of Pennsylvania Department of Physics ATTN: Dr. J.B. Danese Philadelphia, PA 19174
1	University of Rochester Department of Chemistry ATTN: Dr. John Bellum Rochester, NY 14627
	<u>Aberdeen Proving Ground</u> Marine Corps Ln Ofc Dir, USAMSAA